



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION IX
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San Francisco, CA 94105

September 28, 2001

Richard Mach, Jr., P.E.
BRAC Environmental Coordinator
for Hunters Point Shipyard
Southwest Division, Naval Facilities Engineering Command
1220 Pacific Coast Highway
San Diego, CA 92132-5190

RE: **Draft In-Situ Chemical Oxidation Treatability Tests Work Plan Remedial Units RU-2, RU-4, and RU-5 Hunters Point Shipyard, San Francisco, California, August 28, 2001**

Dear Rich,

Please find attached EPA's review of: "Draft In-Situ Chemical Oxidation Treatability Tests Work Plan Remedial Units RU-2, RU-4, and RU-5 Hunters Point Shipyard, San Francisco, California, August 28, 2001." Some of our major concerns with this planned treatability study are listed below. For example, it is recommended that:

- the last phase of the bench-scale treatability study be completed prior to initiating field efforts.
- steps be taken to prevent the accumulation of subsurface vapors and to minimize potential explosive hazards during field implementation.
- subsequent versions of this document contain sufficient detail to assure elected officials and the public that these tests will not result in releases to the environment and/or the San Francisco Bay.
- an assessment be conducted to assure that this field effort will not result in blocked pore space in contaminated soils which may limit future remedial options.

We assume that the Navy will not initiate field work until our major concerns have been addressed. Please feel free to contact me at 415-744-2392 if you have any questions or comments.

Sincerely,

A handwritten signature in black ink, which appears to read "Michael Work".

Michael Work
Remedial Project Manager
Superfund Division (SFD-8-3)

Attachment

cc: (see Distribution List)

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**EPA Comments on the
In-Situ Chemical Oxidation Treatability Tests Work Plan,
Remedial Units RU-2, RU-4, and RU-5
Hunters Point Shipyard
August 28, 2001**

GENERAL COMMENTS

1. A Treatability study was conducted involving the Fenton oxidation of contaminated sediments from RU-4. Although the study was completed, the data were not compiled, assimilated and interpreted and a final report was not prepared. Please provide the results of this Treatability study.

2. The following comment was provided in a previous (October 2, 2000) technical review memorandum and is still applicable to this site.

"Based on an overall analysis of chemical oxidation, many of the potential limitations of chemical oxidation exist at this site, (1) metals mobilization, (2) scavenging, (3) non-productive reactions, (4) insufficient Fe, and (5) sub-optimal pH. The potential role of these limitations can be investigated at bench-scale. Since most of the target compounds in the study area are volatile, volatilization (and loss) of the contaminants in the bench-scale study must be quantified to differentiate volatile from oxidative losses."

It is entirely possible that underlying sediments at site RU-4 are not amenable to chemical oxidation given the potential limitations identified. Presently, the data probably exist by which to make such determination, but have not been adequately evaluated. Therefore, it is recommended that the last phase of the bench-scale Treatability study (data interpretation, data presentation, final report) be completed. Please present the results of the bench-scale Treatability study.

No supporting information from the permanganate bench-scale tests is provided. The only mention of these is in section 2.3.5.1: "The bench scale tests did not indicate efficient oxidation of the chlorobenzene or dichlorobenzene isomers." It is recommended that results from the bench-scale tests be provided and discussed to justify the decisions made in the plan. Additionally, background permanganate oxidant demand was measured but not used in the calculations or design of the oxidant dosage. Please present this information.

3. Well locations and screened intervals have been proposed for areas RU-2, -4 and -5. However, the rationale for the areal and vertical extent of the targeted zones, and the ability of the proposed well locations to deliver the oxidant to the targeted area have not been established. It is recommended that the rationale for the areal and vertical intervals selected for injection be presented. Please provide contaminant mass (ground water, soil) distribution data (isochores) to support the rationale. This applies not only to the horizontal extent but also to the upper and lower vertical extent of contamination.
4. Oxidant volumes for each RU are calculated using average ground water concentrations and assumed non-aqueous phase liquid (NAPL) saturation values and distribution. However, there are monitoring and injection wells that have much higher and lower contaminant concentrations than the calculated average concentration. In conjunction with the previous recommendation, it is recommended that oxidant mass delivery be targeted according to the spatial distribution of contaminants. Please review the spatial distribution of contaminants and revise the mass delivery to target more contaminated zones.
5. No information is presented on performance monitoring, since the plan indicates that information is to be provided in a separate plan submitted by Tetra Tech EM, Inc. However, in a September 24 conference call

between EPA Region 9, Tech Law (an EPA Region 9 contractor) the Navy, and EPA's Kerr Lab, it was indicated that no new plan would be prepared and performance monitoring would be conducted according to the previous (October 20, 2000) work plan prepared by IT Corp. The previous work plan is very general and does not contain details. It is recommended that a current performance monitoring plan be prepared by a current contractor to clarify the performance monitoring. This should clearly explain, for example, the monitoring locations and depths, sampling schedules, and measurement parameters. This will also help to clarify inconsistencies between sections in the October 20, 2000 work plan, such as the sampling schedules and to incorporate deficiencies noted in this review. Only some details are currently available, for example, sampling locations by examining Figures 2-1, 2-3, and 2-4. Without a clear, detailed performance monitoring plan, it is difficult to determine if the pilot field tests will be adequate for establishing the suitability and performance of in situ chemical oxidation for the site. Please provide a performance monitoring plan that includes monitoring locations, depths, sampling schedules and measurement parameters.

6. Due to the potential for volatilization of flammable compounds and high $O_2(g)$ concentrations, an explosion hazard exists at RU-4. It is recommended that steps be taken to take precautions against the potential accumulation of vapors. Please review the potential for vapor accumulation and explosion hazards, and then discuss these issues.
7. This document does not contain sufficient detail to reassure elected officials and the general public that the Treatability tests will not result in releases to the environment (e.g., to air, to San Francisco Bay, etc.). It is unclear how the extent of the areas impacted by treatment will be monitored and controlled. Please provide a contingency plan containing specific procedures to address issues such as avoiding releases to the Bay, avoiding air quality violations, and avoiding uncontrolled reactions that could result in fires or explosions similar to those that occurred in Cherry Point, New Jersey. Please include sufficient groundwater monitoring to evaluate whether groundwater levels rise in the vicinity of the treatment areas, whether the groundwater gradient increases as a result of the injection of reagents, and sampling to evaluate whether contaminants are mobilized as a result of the injection of reagents in a contingency plan, which could be incorporated into the performance monitoring plan. Please discuss how groundwater monitoring will be conducted. Also, please discuss how increased levels of manganese in the subsurface will be minimized.
8. The discussion of the extent of contamination at each of the remedial units (RUs) only focuses on the extent of contamination in groundwater. For RU-4, the discussion only focuses on the extent of contamination in the bedrock aquifer. If the potassium permanganate ($KMnO_4$) or Fenton's reagent cause water levels to rise, then contaminants in the A-aquifer (in the case of RU-4) and the vadose zone may also be treated; this would likely reduce the effectiveness of the treatment in the target zone. Please discuss the extent of contamination in the vadose zone at each of the RUs and in the A-aquifer for RU-4. Also, please discuss how treatment of contaminants in the vadose zone at each of the RUs and in the A-aquifer at RU-4 could reduce the effectiveness of treatment in the target zones, and specify the additional volume of reagents that may be required.
9. It is unclear how the extent of the treated areas will be determined at each RU. For example, there do not appear to be sufficient monitor wells to evaluate whether heterogeneity and anisotropy in the subsurface would result in the creation of preferential pathways or otherwise limit the effectiveness of treatment or how the potential for treatment in overlying layers will be evaluated. Please discuss how the extent of the treated areas will be determined, including specific wells and piezometers that will be sampled. Discuss whether additional monitor wells or piezometers are necessary to provide a more complete evaluation.
10. The effectiveness of the partially completed $KMnO_4$ treatment test at RU-2 should be assessed before further work is done. The questions that should be answered include:

- a. Is there any evidence to indicate that KMnO_4 is effective in treating the contamination at RU-2? Has there been a decrease in contaminant concentration?
- b. What is the impact of manganese dioxide (MnO_2) precipitation on the aquifer? Slug tests and/or pump tests should be conducted in the injection wells and nearby monitor wells to evaluate whether the pore spaces are being blocked by precipitate.

Please evaluate the effect of the partially completed test before proceeding to add more KMnO_4 to the aquifer.

11. As KMnO_4 is converted to MnO_2 , the MnO_2 will precipitate out, blocking pore spaces. Also, after permanganate has been injected, there is no longer a second optional method (for peroxide injection). Residual permanganate will cause vigorous and total decomposition of peroxide to oxygen and water if it was to be injected subsequently. This would make future remediation difficult, if not impossible. Please address how the extent of blocked pore space will be assessed and discuss the limitations for future remediation.
12. It was reported that the background oxidant demand is typically a ratio of about 5 times the stoichiometric demand. Further, estimates regarding the mass of contaminants present in the study area were used in conjunction with the background demand to estimate the total oxidant demand. There were several assumptions used in this analysis that cannot be verified. For example, it was assumed that there is $\frac{1}{2}$ " of DNAPL present at RU-2 but no rationale was presented upon which to base this assumption. Therefore, it is recommended that the estimated mass of oxidant be considered a "working estimate". It is possible that additional oxidant may be needed. The decision to use additional oxidant should be based on data derived from the post-oxidation ground water monitoring program. Please clarify this issue for all three remedial units in the workplan.

SPECIFIC COMMENTS

13. **Section 1.1, Treatability Study Objectives and Rationale, Page 3:** Permanganate, usually injected at a dilute concentration (2, 3 or 4%) is primarily an aqueous phase oxidant, and lacks a forcing agent to effectively/rapidly force desorption of strongly adsorbed or intrapore DNAPL at the adsorbed site (particle or interstice). Enhancing desorption using "persulfuric" acid co-injection has been recently attempted however, the "jury is still out" on this one. Permanganate oxidation is also limited to reactions of unsaturated double bonded molecules and unreactive for trichloroethane (TCA) and dichloroethane (DCA) for example. Fenton-like radicals (superoxide, hydroperoxyl anion, perhydroxyl radical) are thought to be relatively long lived (compared to the fleeting but highly reactive hydroxyl radical) and capable of penetrating the adsorbed DNAPL itself, reacting "insitu", and relatively strong peroxide solutions (10+%) generate significant heats of dilution and reaction with organic subsurface materials and contaminants. This heat of reaction can significantly change surface tension and viscosity characteristics of aquifer fluids (water and contaminants). Please discuss the effectiveness of permanganate on DNAPL and the impact of Fenton's reaction on water and contaminants in the aquifer.
14. **Section 1.3.1, Fenton's Reagent, Page 4:** A classical Fenton's reagent is a very dilute and very well mixed combination of hydrogen peroxide (100 ppm range) and ferrous ions (so-called catalyst) in an acid solution of nominally pH 2-3 SU. Dumping strong solutions of peroxide, with or without ferrous ions will produce a "Fenton's broth" for a short period only at certain boundary regions of the injector location. Local inorganic oxides and organic enzymes/ super oxide dismutases also can have a marked effect on the peroxide and hydroxyl free radical concentration (manganese oxides, etc. will cause rapid decomposition

of peroxide to water and oxygen and, perhaps, some superoxide). Please clarify how Fenton's reagent will be injected into the aquifer and discuss whether areas beyond the injectors will be treated.

15. **Section 1.3.1, Fenton's Reagent, Page 5:** The reaction chemistry shown is somewhat misleading as an excess of peroxide and ferrous ions will act as free radical sinks (also natural catalase type enzymes, superoxide dismutase, and organic/humic materials), removing them from the reactive mix. Many other ions act as radical sinks, an extremely efficient one being (bi-)carbonate - $(\text{H})\text{CO}_3^-$ - from dissolved CO_2 and natural (alkalinity) compounds such Fe/MgCO_3 and bicarbonates). Hydroxyl radicals are very short lived and non-selective in terms of reactions, however strongly adsorbed DNAPL, is not a typical reaction. However the thermal aspects (with possible assistance from generated CO_2) will likely produce dissolution of DNAPL, together with complete degradation of the host adsorbing particle or reacting associated adsorbed organic/humic material. In addition, strong peroxide solutions produce a variety of free radicals and reactive anions, superoxides, organic free radicals, etc. that remedial site experience with peroxide shows the injected "Fenton's broth" to be very effective in source reduction of bulk contaminant mass. Please discuss the impact of excess peroxide and ferrous ions and the possible reactions that may occur.
16. **Section 1.3.1, Fenton's Reagent, Page 5:** It was reported that effective but not optimal oxidation can occur at pH 6. Two references were cited as supportive evidence of this observation. These references do not appear to contain such information. There are several citations in the refereed literature which suggest that very little or no oxidation occurs at pH 6 or above. Please clarify this issue.
17. **Section 1.3.1, Fenton's Reagent, Page 6:** Reaction rates with "catalyzed" peroxide of $1\text{E}9/\text{E}10$ per mole/sec indicate the reactions are generally diffusion controlled and not reaction rate limited. Please revise the text to clarify that reactions are generally diffusion controlled and not reaction rate limited.
18. **Section 1.3.1, Fenton's Reagent, Page 6:** It was reported that 100% mineralization of common environmental pollutants is generally complete in minutes, and CO_2 , H_2O , and Cl^- are the final products. This statement is misleading. Complete mineralization may be demonstrated to occur under ideal conditions such as those employed in the laboratory study conducted by Leung *et al.* (1992) or other similar publications. For example, the solution was prepared with 2.1 M (71,400 mg/L) H_2O_2 , no solid phase organic matter was present for the contaminant to adsorb, no solid phase sediment was present (other than inert silica sand) which may react with H_2O_2 without yielding $\cdot\text{OH}$, the pH was adjusted to optimum (pH 3), Fe^{+2} was present in very high concentrations (5 mM FeSO_4) which optimized the Fenton reaction, complete mix of the solution optimized mass transfer, no significant scavenger concentration was present other than H_2O_2 , and no other reactants with H_2O_2 were present. Under these ideal condition, oxidation of aqueous phase PCE is optimum and complete mineralization is possible. However, in the subsurface system, these conditions simply do not exist. This is discussed in detail below. EPA is unaware of any site or any refereed publication where complete mineralization has been demonstrated to occur in a subsurface system where Fenton oxidation has been used. Correspondingly, it is reasonable to expect that in subsurface systems, partial oxidation and incomplete mineralization of the target compounds will occur. Since it is certain that some of the target compounds will not be oxidized and that some organic compounds will be produced as a byproduct of oxidation, a more accurate overview would reflect this condition. Specifically, please discuss (1) that non-ideal conditions exist in the subsurface, (2) that partial oxidation and incomplete mineralization will occur, and (3) the list of Fenton-based transformation byproducts will include "other organic byproducts."
19. **Section 1.3.1, Fenton's Reagent:** There was no discussion of the effects of heat and gas released with H_2O_2 injection. One side effect is the enhancement of volatilization of VOCs in the source area. Capture of volatiles is important to minimize the redistribution of contaminants. Oxygen gas blockage of ground water flow and contaminant transport, enhanced transport of contaminated ground water, and mobilization of DNAPLs are other effects that have not been addressed. Please discuss these issues.

20. **Section 1.4, General Site Geology and Hydrogeology:** Inclusion of schematics of appropriate geological profiles/cross sections and groundwater flow in the target remedial area(s) would be much more helpful than the reiteration of information in prior RI/FS documents. An interpretation of what this geology/hydrogeology scientific information in section 1.4 means to the oxidation contractor would have been helpful, particularly in terms of the potential for communication between aquifers where the aquitard is discontinuous. Please include cross-sections and groundwater flow maps and discuss the implications of the geology and hydrogeology for the Treatability studies.
21. **Section 2.1.3 Site Layout, Page 16:** It is unclear why IR28IW901A is not specified as being a monitoring well for the proposed test in Figure 2-1 RU-2 Site Layout Map. This well is in the area of highest chlorinated solvent contamination. Please sample this well.
22. **Section 2.1.5.2, Injector Installation, Page 18:** Replacement of the two former injection wells with injection wells located away from the clean solvent line is proposed. The new injection wells have 5' screened intervals. However, it was assumed in the design of the injection program that the targeted interval is 12 ft. It is unclear how oxidant can be delivered across the entire vertical interval if it is injected over 5 ft intervals. It is recommended that the wells be screened over 10 - 12 ft and/or more wells be installed to assure more uniform application of permanganate. Please reevaluate the screen lengths and clarify this issue.
23. **Section 2.1.5.3, Oxidant Delivery Method, Page 18:** The plan does not include checking water levels in monitoring wells to ensure that the water level does not reach the invert elevation of the storm sewer; this was promised by the Navy during a Base Closure Team meeting. Please include monitoring water levels, including an alarm system, if possible so that conditions during the previous test that led to discharge of KMnO_4 to the Bay can be avoided.
24. **Section 2.1.5.3 Oxidant Delivery Method, Page 18:** Installation of a packer in the storm sewer at RU-2 is a good precaution. However, it is important to recognize that potential preferential flow paths such as the material surrounding sewer, utility, and drain lines may also exist at each RU. Please discuss precautions that will be taken to evaluate and minimize groundwater transport via other preferential flow pathways.
25. **Table 2-2:** There is a typographic error in Table 2-2. The DNAPL thickness was designated as zero instead of 0.04 feet.
26. **Section 2.1.5.4 Oxidant Volume, Page 19:** Please state the basis for the assumption that free DNAPL is present in a 20 by 20 foot area.
27. **Section 2.1.5.4 Oxidant Volume, Page 19:** The estimated pore volume in the study area was 78,540 gallons. However, only a total of 33,500 gallons are to be injected. This is approximately 43% of the pore volume. This suggests that 57% of the pore volume will not be contacted. In reality, a much greater percentage will not be contacted due to non-ideal transport mechanisms, such as preferential pathways. It is recommended that a larger volume of permanganate solution be delivered in to the subsurface. For example, a 25 - 30 % greater volume (98,175 - 102,102 gal) may suffice. It may be appropriate to use a lower permanganate concentration in a larger volume of injectate. Please consider using a greater volume of solution and discuss whether a lower concentration of permanganate could be used.
28. **Section 2.1.5.4, Oxidant Volume, Page 19:** The excess of stoichiometric permanganate (5x, table 2-2) assumes a much greater likelihood of efficient contact and reaction than EPA would anticipate for the free phase and soil phase, unless it is quoted to be injected in several sequential passes. Typically a probable minimum of 3 passes (over a lengthy period) will be required to react all but the aqueous phase DNAPL.

Please consider injecting permanganate in three passes, or explain why this will not be done.

29. **Section 2.1.5.4, Oxidant Volume, Page 20:** A total of 33,500 gallons of solution is to be injected, occupying 4,474 cubic feet of space and approximately 18,000 cubic feet of pore volume at the assumed 25% porosity, corresponding to 1489 square foot of area with a thickness of 12 feet. Where the interstitial water that already occupies this space and incoming groundwater will go needs to be established. It is possible that contaminated groundwater will be mobilized when the solution is injected. Water levels, groundwater gradients, and contaminant concentrations in wells located both within and surrounding the treatment area must be monitored. Please revise the plan to ensure that water levels, groundwater gradients and contaminant concentrations will be monitored so that contaminants are not transported to uncontaminated areas or to San Francisco Bay.
30. **Section 2.2.1, Site Location and History, Page 20:** The former solvent tanks are not shown on the referenced figures. Please include the location of the former solvent tanks on Figure 2-3.
31. **Section 2.2.2 Site Geology and Hydrogeology, Page 21:** It is reported that one well located east of the treatment area is located in the A aquifer. However, this well does not appear to be shown on Figure 2-3, unless IR28MW311A is the referenced well. Please clarify or include the well on Figure 2-3.
32. **Section 2.2.2 Site Geology and Hydrogeology, Page 21:** Please provide cross-sections, contaminant concentration plots and discuss them in the text.
33. **Section 2.2.2 Site Geology and Hydrogeology, Page 21:** It is reported that the bedrock water bearing zone is targeted for treatment at RU-4, and that the artificial fill extends 5-10 ft below ground surface. Data in Table 2-3 strongly indicate that the artificial fill is significantly contaminated. In fact, it is unclear if soil near the ground surface becomes uncontaminated. Please present rationale to explain why the artificial fill is not targeted for oxidation in this location.
34. **Section 2.2.3, Site Layout, Page 21:** Please specify how much of the site is paved; this will clarify the potential effectiveness of the Soil Vapor Extraction (SVE) system.
35. **Section 2.2.3, Site Layout, Page 21:** Based on Figure 2-3, the vacuum extraction wells are not located in the same area as the Fenton oxidation injection wells. Assuming enhanced volatilization of the VOCs does occur, the vacuum extraction system is needed to recover the vapors in the area from which they originate. Presently, it is unclear whether the existing vacuum extraction wells can effectively recover volatiles in the proposed oxidation area. Please clarify this issue.
36. **Section 2.2.4 Pre-Test Groundwater Analytical Results, Page 22:** The areal extent of the contamination has not been presented in this report. Specifically, the targeted zone of contamination in conjunction with the areal extent of contamination have not been identified. It is important to identify the areal extent of contamination to appropriately identify the targeted zones of oxidation, and to identify uncontaminated areas to compare to post-oxidation concentrations. Please present and discuss the areal extent of contamination.
37. **Section 2.2.4 Pre-Test Groundwater Analytical Results, Page 22:** The presence of TCE at significant ppm levels, with virtually no other solvent or degradation byproduct, in the presence of relatively high petroleum contaminant concentrations (see also table 2-3; also compare with the data in table 2-1) which should promote co-metabolic processes (as indicated for RU-2) and dehalogenation to include cis DCE (at least) is strange. Perhaps the analytical results indicate that IR28MW211F and the 900 series bedrock wells are not hydraulically interconnected. Please discuss whether the bedrock wells are interconnected and consider the implications of this on the Treatability study. Also please clarify if IR28IW938 (in the

last sentence) should actually be IR28MW938.

38. **Section 2.2.5, Treatability Test Design, Page 22:** It is unclear how treatment will be limited to the bedrock zone, when it is likely that bedrock fractures are hydraulically connected to overburden. Please specify how the reaction will be confined to bedrock, including a discussion of whether the Fenton's reagent will be injected under pressure.
39. **Section 2.2.5, Treatability Test Design, Page 22:** Since Fenton's reagent only works efficiently when the pH is less than 4, please discuss how the pH of the groundwater will be controlled. Please discuss how will the acid to adjust the pH will be introduced into the groundwater, specify the concentration to be used, and discuss how this will be injected into the aquifer with the peroxide to efficiently destroy target compounds. Also, discuss the impact of ferric oxide precipitates on the bedrock fractures.
40. **Section 2.2.5.1 Chemical Oxidation Selection, Page 22:** It was reported that 1,1,2-trichloroethane (1.5×10^8 L/mol-s) and 1,2-DCA are susceptible to Fenton oxidation. However, their reaction rate constants are low and they are present at much lower concentration than other more reactive scavengers and contaminants. It is likely that these compounds will volatilize before they are oxidized under the conditions of this system. Other compounds present at this site, carbon tetrachloride and chloroform, are present at much higher concentrations than 1,1,2-TCA and 1,2-DCA and will not be oxidized via the Fenton reaction. Therefore, selection of Fenton reaction over permanganate is somewhat arbitrary since the reactivity of Fenton and permanganate are approximately the same. However, potential mobilization of contaminants using Fenton based oxidation presents a significant risk. Please clearly discuss why Fenton's reaction was selected.
41. **Section 2.2.5.2 Injector Installation, Page 23:** It was reported that injectors have 5 - 10 ft well screens installed 10 - 20 ft below ground surface. However, the artificial fill is highly contaminated yet is not targeted for oxidation. It is recommended that both the artificial fill and the bedrock water bearing zone be targeted. Correspondingly, the screened interval of the injectors should be more shallow.
42. **Section 2.2.5.4 Oxidant Volume, Pages 23 and 24:** Based on calculations using parameter values reported in this document, 18 pore volumes of oxygen gas [$O_2(g)$] will be released when the H_2O_2 is injected (parameter values: 35,200 lb H_2O_2 , 3500 ft² area, 12 ft thick, 0.25 porosity, mole $O_2/2$ mole H_2O_2). Due to the significant inefficiency of oxidation anticipated to occur at this site, much more H_2O_2 will be required to accomplish the treatment objective than estimated in this section. Therefore, the extent of $O_2(g)$ released will be much greater than the 18 pore volumes currently estimated.

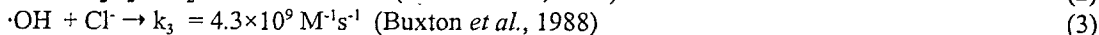
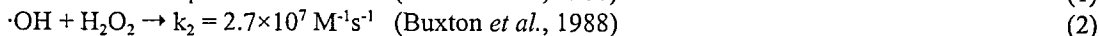
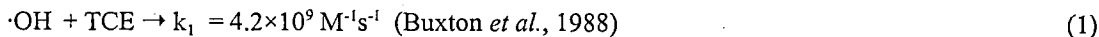
The release of this quantity of $O_2(g)$ and the associated heat from exothermic reactions will have a significant impact on the fate and transport of contaminants at this site. For example, contaminated water in the injection area may be pneumatically transported into adjacent areas which may not be contaminated. Enhanced volatilization and redistribution of the volatiles in previously uncontaminated areas may occur. More importantly, the release of heat and $O_2(g)$ in the source area may mobilize DNAPL. DNAPL is the primary source of contaminants at this site and mobilization, possibly deeper into the fractured bedrock may extend the remedial costs and timeframes. Please discuss the impact of enhanced volatilization, redistribution of volatiles, and potential mobilization of DNAPL.

As indicated in Section 2.2.5.1, the selection of Fenton reaction over permanganate appears to be somewhat arbitrary since the reactivity of Fenton and permanganate are approximately the same. *Overall, it is recommended that Fenton oxidation not be used at RU-4.* However, if it is used, it is recommended that a series of new or existing sentry wells be established which are uncontaminated or show very little contamination. Pre-oxidation baseline contaminant concentrations should be established to compare to the post-oxidation concentration values. Such a comparison will reveal whether the contamination is

redistributed into uncontaminated areas or is degraded.

43. **Section 2.2.5.3, Oxidant Delivery Method, Page 23:** If the injection of Fenton's reagent causes water levels to rise, it is possible that reactions could occur in both the A-Aquifer and the vadose zone. In Cherry Point, New Jersey, use of Fenton's reagent caused fires and explosions when reagent was injected into the aquifer and gasoline range organics (GRO) were present at unknown concentrations in the vadose zone. There appears to be no plan to monitor water levels in bedrock and A-aquifer wells to evaluate whether the injection of oxidant has the potential to impact the A-aquifer and the vadose zone. Please include water level monitoring, with an alarm system, if possible so that conditions can be carefully monitored. Also, please discuss GRO concentrations in the A-aquifer and vadose zone and explain how conditions similar to those in Cherry Point will be avoided. Finally, if reactions occur in the A-aquifer and in the vadose zone, additional reagent may be necessary. Please discuss whether the amount of reagent will be sufficient if reactions occur in the A-aquifer.
44. **Section 2.2.5.4 Oxidant Volume, Pages 23 and 24:** It was reported that an additional factor (3-5) must be considered for H_2O_2 demand from oxidizable TOC and metals in ground water plus natural inefficiencies. The factor cited by GeoCleanse at other sites has not been documented and is not supported by an oxidation kinetic analysis.

A simple kinetic analysis using site specific data can be used to demonstrate that the hydroxyl radical mediated process is less efficient than suggested by the factor of 3-5 presented in the report indicated by GeoCleanse Inc. the stoichiometry suggests:



The average TCE concentration reported in Table 2-3 is 13.5 mg/L, Cl^- concentration is 220 mg/L and H_2O_2 is 50%. Assuming the only reactants in the system were H_2O_2 , Cl^- , and TCE, the relative rate of reaction of H_2O_2 and Cl^- , versus TCE can be estimated as follows.

$$(dH_2O_2/dt) / (dTCE/dt) = [H_2O_2] k_2 [Cl^-] k_3 / [TCE] k_1 = 990$$

Results suggest the rate of reaction between H_2O_2 or Cl^- and $\cdot OH$ is 990 times faster than that between TCE and $\cdot OH$. As the concentration of TCE declines, and additional applications of H_2O_2 occur, the rate of scavenging and process inefficiency increase. Similar calculations involving this simplified competition kinetic analysis and other sources of process inefficiency (non-productive reactions, suboptimal pH, insufficient Fe) have been reported (Huling *et al.*, 1998) and would be expected to occur at this site.

A factor of 3 - 5 used to estimate process inefficiency and H_2O_2 dosing requirement is an underestimate of process inefficiency. Please consider using at least 10 times the stoichiometric peroxide molar equivalent, and consider applying the reagents in 3 passes, conducted over a period of time.

45. **Section 2.2.5.4 Oxidant Volume, Pages 23 and 24:** No information was provided regarding the type and quantity of other injected materials that would be used. For example, iron would not be expected to be available naturally in the presence of saltwater intrusion, so iron should be injected. Please specify the volume and concentration of each chemical to be injected. Then, given the total volume of chemicals to be injected, consider where the water displaced by the injected material will go. Please provide sufficient groundwater monitoring so that the potential increase in water levels, increased hydraulic gradient and possible contaminant mobilization can be monitored.

46. **Section 2.3.5.1 Chemical Oxidant Selection, Page 27:** The predominant contaminants at RU-5 are 1,2-dichlorobenzene (1,800 µg/L), 1,4-dichlorobenzene (940 µg/L), chlorobenzene (9,900 µg/L), CIS (910 µg/L), and VC (665 µg/L). Despite the bench-scale tests not indicating efficient oxidation of the chlorobenzene or dichlorobenzene isomers, apparently using permanganate, permanganate oxidation has been selected for RU-5. There does not seem to be any clear rationale for testing a technology that will not address a significant portion of the contaminants. If the site is intended as a research project rather than a remediation project, then the stated rationale of testing different injection methods might be understandable; however, if the intent is to remediate the site, it is recommended that the choice of technology be re-evaluated. A modified Fenton's system, using strong peroxide solutions (> 2% after injection/dilution with GW) should be effective on the chlorinated solvents and the petroleum type contaminants. Please justify the selection of permanganate for RU-5.
47. **Section 2.3.5.3, Oxidant Delivery Method, Page 28 and Section 3.3.1, Direct Push Injection, Page 35:** It is unclear whether injection will occur in more than one direct push location at a time or whether will be possible to go back to a direct push location and inject additional oxidant, which could be necessary if a location does not accept a sufficient quantity of KMnO_4 . Please clarify whether injection will occur in more than one location at a time and whether additional oxidant can be injected later. Please discuss procedures to be followed if a direct push location does not accept a sufficient quantity of KMnO_4 . Also, please discuss whether injection is planned at the full 30 gallons/minute capacity of the pump.
48. **Section 2.3.5.3, Oxidant Delivery Method, Page 28:** The text does not include checking water levels in monitoring wells to ensure that the water level does not reach the invert elevation of local storm sewers; this was promised by the Navy during a Base Closure Team meeting. Please include monitoring water levels, including an alarm system, if possible so that conditions during the previous test that led to discharge of KMnO_4 to the Bay can be avoided.
49. **Section 2.3.5.4, Oxidant Volume, Page 28:** In the last paragraph, it states that "a ratio of 3 lbs KMnO_4 per 1 lb of VOC is utilized." The calculations in Table 2-6 use 2.87 lbs KMnO_4 per 1 lb of VOC. Please resolve this discrepancy.
50. **Section 3.1.3, Chemical Laydown Area, Page 31:** Please include the location of this area on Figure 1-1. Please note that the chemical oxidants and reductants (bisulfite) should be fully restrained from any possible commingling in the Chemical Laydown Area, particularly at reagent purchase strengths. Contact may be particularly vigorous. Also, it is unclear what provisions have been made for the iron catalyst and pH adjustment necessary for the Fenton's reagent for RU-4. Please describe storage of the Fenton's reagents and discuss how the acid will be neutralized in the event of a spill.
51. **Section 3.3.2, Fixed Well Injection, Pages 35 and 36:** It is unclear if the packers for the injectors will be moved so that injection into different zones of the screened interval can be evaluated. Please clarify whether the packers will be moved, and if not, discuss how injection into less permeable layers will be accomplished.
52. **Section 3.3.2, Fixed Well Injection, Page 35:** Mixing heads and injectors are discussed, but no information concerning premixing reagents prior to subsurface injection is provided. Please specify the reagents to be used and how they will be mixed.
53. **Section 3.4 Process Monitoring:** The locations of samples to be collected for process monitoring are not defined, other than "within and adjacent to the treatment area", and it is not clear if the monitoring wells shown in Figures 2-1, 2-3, and 2-4 are for process monitoring, performance monitoring, or both. Please clearly specify the locations and depths of samples.

54. **Section 3.4, Process Monitoring, Pages 36, 37 and 39:** Production of gas during a Treatability test is first mentioned in the first full paragraph on Page 37. Please explain how gas pressure will be monitored, how often it will be monitored and how excess pressure in headspaces and monitoring wells will be relieved. Also, please discuss how sufficient venting will be provided to ensure that there is no buildup of gas in the subsurface.
55. **Section 3.4, Process Monitoring, Pages 36, 37 and 39:** Please discuss Bay Area Air Quality Management District (BAAQMD) air quality standards; and specify the amount of each chemical of concern, including those in the A-aquifer and vadose zone, that can be released. Please discuss how monitoring will be conducted, how quickly analytical results can be obtained and what will be done to avoid violating air quality standards. Also, discuss procedures to be followed if it is known or suspected that the quantity of gas will exceed air quality standards.
56. **Section 3.4, Process Monitoring, Page 36:** Process monitoring should include monitoring water levels in all available monitoring wells and piezometers, so that any changes in water level and changes in groundwater hydraulic gradients can be carefully monitored. Please include water level monitoring and groundwater hydraulic gradient calculations as part of process monitoring.
57. **Section 3.4.1 Fenton's Reagent Process monitoring, Page 37:** It was not reported how the pH was to be altered and maintained. Please clarify this issue. Additionally, it was proposed to maintain the pH less than pH 6. It should be noted that at pH 6, chemical oxidation efficiency is very low. Oxidation efficiency is optimum in the pH range of 2.5 to 3.5. The Hach test kit would not be useful for this range. Please reevaluate the need to maintain a lower pH to increase oxidation efficiency and specify how the pH will be determined.
58. **Section 3.4.1 Fenton's Reagent Process monitoring, Page 38:** The background chloride (Cl^-) concentration is approximately 220 mg/L (i.e. 0.554×0.4 ppt) and oxidation of uncontaminated sediments will release additional Cl^- . Therefore, it is unclear whether Cl^- release from contaminant oxidation can be differentiated from background Cl^- at this site. Please clarify this issue.
59. **Section 3.4.1 Fenton's Reagent Process monitoring, Pages 38 and 39:** The text states that CO_2 and O_2 are sensitive measures of reaction progress and efficiency. However, there are limitations. Oxygen, a byproduct from the Fenton reaction and produced in large quantity, will clearly be present in the subsurface. Dissolved oxygen (DO) will reach near saturation levels, but the data cannot be used to quantify treatment because $\text{O}_2(\text{g})$ will be produced and DO will increase whether contaminants are oxidized or not. Further, carbonate in ground water (measured as alkalinity) serves as both a source and sink for free CO_2 . CO_2 can be produced simply from the acidification of carbonates (HCO_3^- , CO_3^{2-}). Since GCI injects an acid solution with the H_2O_2 , generation of $\text{CO}_2(\text{g})$ will result. Assuming the VOC's were partially mineralized, it would be difficult, if not impossible to differentiate CO_2 produced between HCO_3^- and CO_3^{2-} acidification from VOC mineralization. $\text{CO}_2(\text{g})$ and $\text{O}_2(\text{g})$ produced and transported into the subsurface are free to move vertically and laterally which is dependent on specific pneumatic forces. Therefore, measurement of $\text{CO}_2(\text{g})$ and $\text{O}_2(\text{g})$ may not be spatially correlated with mineralization. Overall, due to the various sources and sinks of CO_2 , and the ubiquitous nature of $\text{O}_2(\text{g})$ in Fenton systems, they are poor indicators of treatment performance. Please reconsider whether dissolved oxygen and carbon dioxide can be effectively used to monitor treatment performance, and if these parameters will still be measured, please explain how the data will be interpreted and used.
60. **Section 3.5, Performance Monitoring, Page 41:** This section is only one sentence long and does not contain sufficient detail. Please specify when performance monitoring will be conducted, the wells and piezometers that will be sampled, the analyses to be done, and reference the document that will contain the Field Sampling Plan and Quality Assurance Project Plan.

References

- Buxton, G.V., Greenstock, C., Hellman, W.P., Ross, A.B. 1988. Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms, and Hydroxyl Radicals ($\cdot\text{OH}/\cdot\text{O}$) in Aqueous Solution. *J. Phys. Chem. Ref. Data*, 17(2), 513-886.
- Huling, S.G., R.G. Arnold, R.A. Sierka, M.A. Miller. 1998. "Measurement of Hydroxyl Radical Activity in a Soil Slurry Using the Spin Trap α -(4-pyridyl-1-oxide)-N-tert-butyl-nitron." *Environmental Science and Technology*, (32)21, 3436-3441.
- Leung, S.W., R.J. Watts, and G.C. Miller. 1992. "Degradation of Perchloroethylene by Fenton's Reagent: Speciation and Pathway." *Journal of Environmental Quality*, (21) 377-381.